

EVALUATION OF OLIGOMERIC MODELS OF COAL ASPHALTENES AND PREASPHALTENES AS GPC CALIBRATION STANDARDS

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INTRODUCTION

One important facet of the characterization of coal and coal derived materials is that of molecular weight determination. The initial goal of this study was to synthesize a series of model oligomers that were in agreement with the average structural formulas of some selected coal derived asphaltene and preasphaltene samples as determined by proton nuclear magnetic resonance spectroscopy, elemental analyses and various oxygen derivatization procedures. The second goal was to test these model compounds along with some commercially available polystyrene standards as calibration standards for high pressure gel permeation chromatographic procedures. The retention volumes of these model compounds were compared with those volumes for a group of coal derived asphaltene and preasphaltene samples which had been previously isolated by preparative gel permeation chromatographic techniques.

The application of GPC to the characterization of coal derived materials has been studied by a number of researchers (1-13). Coleman et al. (2-3) demonstrated that three column packings; styrene-divinylbenzene (Bio-Beads S-X4), cross-linked poly(acryloylmorpholine), and modified alkylated dextran (Sephadex LH-20) polymers; could be used for the GPC separation of THF and CHCl_3 solvent refined coal (SRC) fractions. Schwager et al. (1) isolated four SRC asphaltene fractions by preparative techniques using Bio-Beads SX8. A linear relationship between the logarithm of number average molecular weight and retention volume was observed using an analytical μ -styragel HPLC column. The analytical column was calibrated with a series of aromatic hydrocarbons, a porphyrin and propylene glycols of known molecular weight. Curtis et al. (4) studied the characteristics of an SRC (Amax) using GPC techniques. The separation employed three μ -styragel columns using THF as the solvent and was calibrated with a series of polyethylene glycol and various polynuclear aromatic hydrocarbon standards. Sephadex LH-20 has also been used to fractionate the hexane soluble portion of the pyridine extract from a Sorachi coal (5). Khan (6) compared the use of GPC and vapor pressure osmometry (VPO) to obtain molecular weight data for the hexane soluble portion of three H-coal liquids. Two packings, polyvinylacetate (Fractogel PVC 500) and styrene-divinylbenzene copolymer (Toyo Soda, G2000H10) were used as analytical columns. Calibration of the columns was accomplished by VPO measurement of number average molecular weight in toluene of preparative scale fractions obtained from a Fractogel column.

All of this work has demonstrated that the quantitative interpretation of GPC chromatograms raises two problems. First, the response of the detector must remain constant on a per weight basis over the molecular range (i.e., type and distribution of chromophores must be constant). A constancy of uv absorbance per gram for a series of SRL materials has been reported in work by Ruud (9). However, this point needs to be investigated more thoroughly. A second problem, which is the focus of this paper, is the establishment of the response curve with suitable calibration standards.

EXPERIMENTAL

Materials

Polystyrene standards used to obtain the reference GPC curve were obtained from Polysciences, Inc. Other standard compounds were synthesized from starting materials obtained from various commercial sources (14). Solvent refined lignite (SRL) samples produced at 460°C, 27.6 MPa (4000 psig) using synthesis gas were obtained from the Grand Forks Energy Technology Center and solvent fractionated to obtain asphaltene and preasphaltene fractions (15). The lignite used was from a North Dakota seam, Beulah three.

Preparative Scale GPC

The SRL asphaltenes and preasphaltenes were further separated using a 50 mm id x 120 cm glass column packed with Bio-Beads S-X3 (200-400 mesh) styrene-divinyl benzene. Prior to GPC separation all the SRL samples were acetylated in order to convert the hydroxyl sites to their acetate forms. Freshly distilled toluene or pyridine was used as the solvent. Typical analytical GPC chromatograms of an asphaltene sample obtained from the preparative column are presented in Figure 1. Elemental analyses of the fractions were performed by Spang Microanalytical Laboratory and number average molecular weights were determined in our laboratory using a Wescan Model 117 Vapor Pressure Osmometer. In normal runs, 2-3 concentrations over the range 1 to 50 g/kg of pyridine were employed for extrapolation to infinite dilution.

Analytical Scale GPC

Analytical scale GPC analyses (HPLC) were carried out using three 10 nm and one 50 nm μ -styragel columns in series, with THF (UV grade, Burdick and Jackson) as the mobile phase. A Laboratory Data Control Model 1205 UV Monitor was used as the detector (254 nm) and a Waters Model UK6 injector was used to inject samples of about 10 μ l at 10 mg/ml. Samples were filtered across a 0.5 μ m millipore filter prior to injection. The flow rate was usually maintained at 1.0 mL/min to prevent pressures in excess of 1000 psig.

RESULTS AND DISCUSSION

The determination of the number average molecular weights of the asphaltene and preasphaltene SRL fractions by vapor pressure osmometry (VPO) makes it possible to establish the experimental relationships between elution volume in the analytical GPC and molecular weight. Band broadening of the peaks as shown in Figure 1 is a function of the number of theoretical plates of the column and the polydispersity of the sample. The column system was found to have 7,500 plates when using pyrene in THF. The polydispersity ratios (M_w/M_n) of the SRL samples were measured using commercial polystyrene for calibration of the molecular weight and retention volumes assuming a linear response. The polydispersity ratio for each of the polystyrene standards was 1.3. The range of polydispersity values of the SRL fractions was found to be 1.05 to 1.3.

Figure 2 shows a plot of the logarithm of molecular weight versus retention volume for the polystyrene standards, the acetylated SRL asphaltenes and preasphaltenes and a series of oligo(aryl ethers) and oligo(aryl methylenes) from 170-570 g/mole. A nearly linear relationship was found provided the aryl moieties were benzenoid. However, deviations from linearity were observed for both model compounds and SRL samples containing more

condensed aromatic nuclei (i.e., naphthalene, phenanthrene and pyrene). Substances containing larger aromatic nuclei were found to elute too late for their molecular weight. The length per molecular weight of these compounds is less than a benzenoid molecule of the same weight. Because of the smaller size these compounds elute at a later time. The fraction of aromatic carbons present as edge carbons ($H_{\text{aru}}/C_{\text{ar}}$) was measured by proton nmr to be 0.63 to 0.90 for the asphaltenes and preasphaltenes. Calculated values of $H_{\text{aru}}/C_{\text{ar}}$ for the model compounds ranged from 0.67 to 1.0 and for the polystyrene standards were 1.0. Those SRL samples with $H_{\text{aru}}/C_{\text{ar}}$ ratios greater than 0.70 gave nearly a coincident linear plot with the polystyrene standards as shown in Figure 2.

Philip and Anthony (12) have shown that when THF is used as a mobile phase species capable of hydrogen bonding result in elutions corresponding to larger molecular size and smaller retention volumes. We observed this effect particularly for 200-300 g/mole model compounds containing a phenolic hydroxyl group. Philip and Anthony (12) also observed that rigid molecules such as polynuclear aromatics have smaller molecular sizes and thus larger retention volumes. The present direction of our research is to prepare a series of condensed aromatic oligomers so we can better match the $H_{\text{aru}}/C_{\text{ar}}$ values of the calibration standards and the coal derived liquids.

CONCLUSIONS

Polystyrene, oligo(phenyl ethers) and/or oligo(phenyl methylenes) are suitable GPC calibration standards for most derivatized SRL asphaltenes and preasphaltenes. More condensed aromatic oligomers (i.e., containing phenanthryl and pyrenyl moieties) may be required for accurate GPC determination of the molecular weights of SRL samples with low $H_{\text{aru}}/C_{\text{ar}}$ (highly condensed aromatics). The SRL samples must be derivatized to block free -OH groups and prevent interaction with the GPC solvent, THF.

ACKNOWLEDGEMENT

The research was supported by DOE through contract number DE-FG22-81PC40810.

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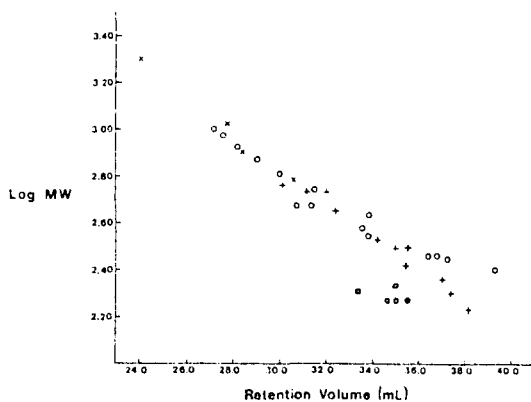


Figure 2. GPC calibration plot. X = polystyrene standards;
 o = SRL samples with $H_{\text{aru}}/C_{\text{ar}} \geq 0.70$; + = model
 compounds with $H_{\text{aru}}/C_{\text{ar}} \geq 0.89$ and without phenolic
 $-OH$; • = model compounds with $H_{\text{aru}}/C_{\text{ar}} \geq 0.89$ and
 with phenolic $-OH$.

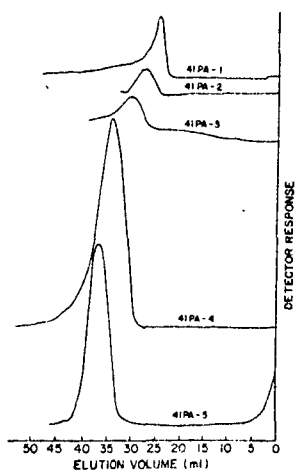


Figure 1. HPLC GPC chromatograms of acetylated SRL
 preasphaltenes separated by preparative GPC.